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(54) **Porous membrane formed from an interpenetrating polymer network having hydrophilic surface**

Poröse Membran hergestellt aus einem interpenetrierenden Polymernetzwerk und mit einer  
hydrophilen Oberfläche

Membrane poreuse fabriquée d'un réseau interpénétré de polymères pourvue d'une surface hydrophile

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<b>EP-A- 0 054 354</b>	<b>EP-A- 0 186 758</b>
<b>EP-A- 0 261 734</b>	<b>US-A- 4 012 324</b>
<b>US-A- 4 119 581</b>	<b>US-A- 4 708 981</b>
<b>US-A- 4 752 624</b>	<b>US-A- 4 787 976</b>
<b>US-B- 276 993</b>	

- **Encyclopedia of Polymeric Science and Engineering, Vol.8, 2nd edition (1987), J.Wiley&Sons, N.Y., USA; pp.279-284 "Interpenetrating polymer networks"**

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

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## Description

## BACKGROUND OF THE INVENTION

This invention relates to a microporous or ultrafiltration membrane having a hydrophilic surface and formed from an semi-interpenetrating network of a hydrophobic polymer and a hydrophilic cross linked monomeric composition and to the process for forming the membrane.

According to Encyc. of Polym. Sci. and Technology, Vol. 8, 2nd ed., J. Wiley & Sons, N.Y., U.S.A., pp. 279-284, an interpenetrating polymer network (IPN) is an intimate combination of two polymers both in network form, at least one of which is synthesized or crosslinked in the intermediate presence of the other (see page 279). A semi-IPN is formed, if one of the two polymers is in network form (crosslinked) and the other a linear polymer, i.e. not crosslinked (see page 283).

In many applications of filtration technology, it is desirable to utilize a membrane filter which is mechanically strong, is thermally stable, is relatively inert chemically and is insoluble in most organic solvents. Often, it is desirable that the membrane has surface properties which are radically different from, and sometimes incompatible with, the bulk properties of the membrane. Desirable surface properties include wettability, low protein adsorbing tendency, thromboresistivity, controlled ion exchange capacity and controlled surface chemical reactivity.

Conventional methodology presently used to achieve the duality of function of bulk properties which differ from the surface properties is to coat a preformed membrane having the desired bulk properties with an oligomer or polymer having the desired surface properties. Typical coating materials include surfactants and water soluble polymers such as polyvinylpyrrolidone. This approach has disadvantages, particularly because the coating reduces flux by reducing pore size; flux reduction is especially severe for small ( $<0.1 \mu\text{m}$ ) pore membranes.

It also has been proposed to utilize graft polymerization techniques to modify the surface characteristics of a polymeric substrate. Typical examples of graft polymerization are shown for example in US-A-3,253,057; US-A-4,151,225; US-A-4,278,777 and US-A-4,311,573. It is difficult to utilize presently available graft polymerization techniques to modify the surface properties of the porous membrane. This is because it is difficult to modify the entire surface of the membrane including the surfaces within the pores while avoiding significant pore blockage and while retaining membrane porosity.

It has been proposed in US-A-4,618,533 to form a porous membrane having a porous membrane substrate to which is directly coated a cross-linked polymer formed from a monomer polymerized with a free radical initiator in situ on the substrate. The resulting composite membrane has essentially the same porous configuration as the porous substrate. It is disclosed that the presence of a polymerization initiator and a cross-linking agent are necessary in order to effect the desired polymerization and cross-linking in situ and thereby to obtain the desired porous configuration of the membrane product, i.e., little or no blockage of the pores, because the pores are large.

US-A-4,119,581 discloses a method for producing an ion-exchange non-porous membrane from a solution of a thermoplastic polymer (fluoro carbons are mentioned) and monomers which is cast in sheet form and, when exposed to heat or gamma radiation, becomes polymerized to form an interpenetrating network of polymer chains. The monomers used to form the ion exchange capacity of the membrane are a diamine and a dihalide. They undergo the Menshutkin reaction to produce inherently ionic polymers.

US-A-4,302,334 discloses a process for making a microporous membrane from a casting solution of a hydrophobic polyvinylidene fluoride preferably of high crystallinity and a vinyl acetate polymer. The resulting polymer blend solution is cast on a substrate in the usual way and coagulated to form a porous membrane. The polyvinyl acetate is then hydrolyzed to polyvinyl alcohol, a hydrophilic polymer.

US-A 4,012,324 discloses a method for making porous membranes from a solution of a polyelectrolyte, a matrix polymeric mixture and a cross-linking agent, e.g., an epoxy. Cross-linking is effected by heating.

The crosslinking groups can be a part of either the matrix polymer or the polyelectrolyte reacting with one another on the same chain. Further, in some formulations a chemical crosslinking reaction can take place between the crosslinking agent and either the matrix polymer or the polyelectrolyte. However, in contrast to the present invention to be described below according to US-A-4 012 324 the hydrophilic polymer is polymerized beforehand and not in the casting solution and the crosslinking step only is carried out after the drying of the cast membrane film.

EP-A-0 261 734 discloses a process for the preparation of hydrophilic membranes by coagulation of a solution of at least one hydrophobic polymer and at least one hydrophilic polymer in a suitable solvent medium on a coagulation medium. A mixed solution of the two polymers is coagulated, dried at higher temperatures and the hydrophilic polymer component is thereafter thermally or chemically crosslinked.

US-A-4 752 624 discloses a process for the preparation of a non-porous interpenetrating polymer network membrane, composed of a hydrophilic and a hydrophobic component.

US-A-4 787 976 discloses a protein non-adsorptive semipermeable filtration membrane comprising an interpenetrating polymer network. The membrane is prepared from a casting solution comprising a hydrophilic urethane prepolymer polymerizable upon contact with a coagulating liquid, a polymer that will not react readily with the prepolymer and that is substantially insoluble in said coagulating bath, and solvent. The solution is cast as a film on a support, the film

then being immersed in a coagulation bath which effects polymerisation of the prepolymer and the formation of the pores. No annealing treatment is mentioned.

The prior art discloses a variety of ways to produce porous hydrophilic membranes from materials that are primarily hydrophobic. None discuss a two step process for producing hydrophilic porous membranes by polymerizing a hydrophilic monomer in a solution of a hydrophobic polymer, subsequently casting a membrane from the solution; and then annealing to produce a hydrophilic membrane.

#### SUMMARY OF THE INVENTION

The present invention provides a water wettable porous membrane formed of a porous semi-interpenetrating polymer network of a hydrophobic fluorinated hydrocarbon polymer and a crosslinked hydrophilic polymer which is formed from a polymerized hydrophilic monomer, the interpenetrating polymer network being formed by synthesizing and crosslinking the hydrophilic polymer in the immediate presence of the hydrophobic polymer, wherein the entire surface of the membrane including the pore surface is formed from said hydrophobic polymer in semi-crystalline form and said hydrophilic polymer. The membrane is formed from a solution of the hydrophobic polymer, a monomeric composition which is a precursor to the hydrophilic polymer, a cross-linking agent for the monomeric composition and a photoinitiator. The solution is cast on a substrate and is exposed to ultraviolet radiation in order to polymerize and cross-link the monomeric composition in order to form an semi-interpenetrating polymeric network in solution. The resultant polymeric solution is coagulated. During coagulation, pores are formed in the membrane and most of the solvent is removed. The remaining solvent is washed out of the membrane in a subsequent washing step. The membrane is then annealed by a heat treatment. Upon annealing, the crystallinity of the hydrophobic polymer is increased and thereby the water wettability of the entire surface of said membrane, including the pore surface is increased. The membranes of this invention can be used without prewetting in filtration processes which process aqueous solutions, such as in the pharmaceutical industry or the electronics industry.

#### DESCRIPTION OF SPECIFIC EMBODIMENTS

The present invention provides a porous membrane having a hydrophilic surface and novel morphology according to claim 1. The membrane is formed from a semi-interpenetrating network of a hydrophobic polymer and a hydrophilic polymer produced by polymerizing and crosslinking a hydrophilic monomer in the immediate presence of the hydrophobic polymer. The surface of the membrane including the pore surface is formed from a mixture of hydrophobic and hydrophilic polymers which renders the overall membrane surface hydrophilic. The hydrophobic polymer is rendered crystalline and the surface is rendered hydrophilic as a result of the annealing step described below. In one aspect of this invention a membrane having a hydrophilic surface and an average pore size within the range of about 0.01 to 0.1  $\mu\text{m}$  (.01 to .1 microns) is provided.

The hydrophobic polymers useful in the present invention are those which are rendered crystalline under the annealing conditions set forth below. Suitable hydrophobic polymers include fluorinated polymers such as polyvinylidene fluoride or the like.

In accordance with this invention, there is provided a porous membrane formed of an semi-interpenetrating polymeric network having the desired bulk properties and a hydrophilic surface. The semi-interpenetrating network of the hydrophobic polymer and hydrophilic polymer is formed from a solution of the hydrophobic polymer, a monomeric composition precursor of the hydrophilic polymer, a cross-linking agent for the monomeric composition and a photoinitiator. The solution is cast onto an appropriate substrate, after which the monomeric composition is polymerized and cross-linked in the cast film by exposure to ultraviolet radiation. The irradiated film then is coagulated to a porous membrane. During coagulation, most of the solvent leaves the membrane; the rest is washed out afterward. The porous membrane is then annealed to make it hydrophilic.

Many monomeric compositions can be utilized herein as long as it is capable of being polymerized by free radical polymerization and can be cross-linked to form a hydrophilic surface on the membrane product. Representative suitable polymerizable monomers include hydroxylalkyl acrylates or methacrylates including 1-hydroxyprop-2-yl acrylate and 2-hydroxyprop-1-yl acrylate, hydroxypropyl methacrylate, 2,3-dihydroxypropyl acrylate, hydroxyethylacrylate, hydroxyethylacrylate, hydroxyethyl methacrylate, N-vinyl pyrrolidone or the like or mixtures thereof.

The particular solvent employed for the hydrophobic polymer and the monomeric composition will depend upon the particular monomeric composition employed and upon the particular hydrophobic polymer utilized to form the porous membrane. All that is necessary is that the monomer, the crosslinker, the initiator, the hydrophobic polymer and the interpenetrating network dissolve in the solvent. Representative suitable solvents include dimethylacetamide (DMAC) or N-methylpyrrolidone (NMP). Generally the polymerizable monomer is present in the solution at a concentration between about 3 and about 15%, preferably between 5 and 10% based upon the weight of the solution. The hydrophobic polymer is present in the solution at a concentration between about 10 and about 20%, preferably between about 12 and about 18%, based upon the weight of the solution. The hydrophobic polymer provides mechanical strength to the

membrane while the hydrophilic polymer provides desirable surface characteristics to a membrane such as protein rejection. If too little hydrophilic polymer is utilized, membrane wettability is undesirably reduced. Excessive hydrophilic polymer results in undesirable gelling and polymer separation. Thus, increased amounts of hydrophilic monomer cannot be utilized as a means to improve the wettability of the membrane surface.

Suitable initiators and cross-linking agents for the monomers set forth above are well-known in the art. For example, when utilizing acrylates as the polymerizable monomer, suitable polymerizable initiators include benzoin ethers such as isopropyl benzoin ether and butyl benzoin ether; benzophenones such as benzophenone and Michler's ketone and acetophenones such as 2-hydroxy-2-methyl phenyl propanone,  $\alpha$ ,  $\alpha$  dimethoxy-  $\alpha$ -phenyl acetophenone and  $\alpha$ ,  $\alpha$ -dimethoxy  $\alpha$ -hydroxy acetophenone or the like. When utilizing acrylates or methacrylates as the polymerizable monomer, suitable cross-linking agents include difunctional acrylates, or methacrylates such as tetraethylene, glycol diacrylate or dimethacrylate. The cross-linking agent generally is present in an amount of between about 5% and about 30% by weight, preferably between about 6% and about 25% by weight based on the weight of the polymerizable monomer. Greater amounts of cross-linking agent can be used but no significant advantage is gained thereby. The polymerization initiator is present in an amount between 2% and 8% by weight, preferably between 3% and 5% by weight based upon the weight of the polymerizable monomer.

After the solution of hydrophobic polymer and monomeric composition is formed, it is cast on a substrate such as glass, polyester or nonwoven fabric or the like to form a film of a thickness generally between 5 and about 15  $\mu\text{m}$  (microns). The film is exposed to ultraviolet radiation of low intensity so as to avoid excessive reaction rates which produce non-uniform polymerization. Typical radiation intensities are between about .2 and about 2  $\text{mW}/\text{cm}^2$  at a wave length between about 350 and about 400 nm for a period of between about 10 and about 120 seconds in order to initiate free radical polymerization and cross-linking of the monomeric composition thereby to effect formation of an semi-interpenetrating polymeric network in solution. The cast film of semi-interpenetrating polymeric network solution is coagulated by putting it into a liquid in which the network is insoluble and with which the solvent is miscible, such as water, alcohols, alcohol-water mixtures, or acetone-water mixtures. Pores form in the membrane during coagulation.

Surprisingly, it has been found that the last step of the process of this invention, i.e., the annealing step, causes the membrane to become easily wettable. That is, the annealed membrane is entirely wettable with an aqueous solution within a time period of less than about 1 minute. Annealing is conducted at a temperature between about 130°C and 150°C for a time between about 20 minutes and 60 minutes. Preferably annealing is conducted while the membrane is restrained to prevent shrinkage. As a result of annealing, the hydrophobic polymer becomes more crystalline. The hydrophilic polymer is excluded from either of these crystalline regions. It covers them and renders the material surface hydrophilic. The hydrophobic polymer is referred to herein as "semi-crystalline". By the term "semi crystalline" as used herein is meant polymeric solids intermediate between true crystals and amorphous structures. Typically they give X-ray patterns with several maxima, with lines sharper than those of liquids.

The membranes of this invention can have a very small maximum pore size of between about 0.01 to 0.1  $\mu\text{m}$  (0.01 to 0.1 microns). Generally, membranes having a pore size this small suffer from serious flux reductions since the ratio of the decreased flux observed between a small pore membrane and a large pore membrane is proportional to the fourth power of the pore size ratio. These small pore membranes of this invention have a flux of at least about 407.5  $\text{hl}/\text{m}^2/\text{d}$  (1000  $\text{gal}/\text{ft}^2/\text{day}$ ) at 172 kPa (25 psi). Despite these very small maximum pore sizes, these membranes have excellent flux characteristics. These very small maximum pore size membranes have isopropyl alcohol bubble pressures or points as defined herein of between about 275 kPa (40 pounds per square inch (psi)) and about 963 kPa (140 psi). Water flux of these membranes is above about 1426  $\text{hl}/\text{m}^2/\text{d}$  (3500 gallons per square foot per day) at 172 kPa (25 psi) (gfd at 25 psi) for these membranes whose bubble point is about 275 kPa (40 psi), decreasing to above about 407.5  $\text{hl}/\text{m}^2/\text{d}$  (1000 gfd) at 172 kPa (25 psi) for membranes whose bubble point is about 550 kPa (80 psi), and also above about 407.5  $\text{hl}/\text{m}^2/\text{d}$  (1000 gfd) at 172 kPa (25 psi) for membranes whose bubble point is about 963 kPa (140 psi) as shown in the figure.

The following examples illustrate the present invention and are not intended to limit the same.

#### EXAMPLE I

A solution was formed from 5 grams of hydroxypropylacrylate monomer, 1.3 grams of tetraethyleneglycoldiacrylate, 4 grams of a photoinitiator comprising Darocure 1173 ( $\alpha$ ,  $\alpha$ -dimethoxy- $\alpha$ -hydroxy acetophenone) available from E. Merck Corporation which were added to 89.7 grams of a 14 weight % solution of poly(vinylidene fluoride) and 5 weight % lithium chloride (LiCl) in dimethylacetamide (DMAc). The solution was cast in a film approximately 254  $\mu\text{m}$  (10 mils) thick on a glass plate and thereafter exposed to ultraviolet radiation wavelength of maximum emission of 365 nm at an intensity of between about 0.2 and 0.6  $\text{mW}/\text{cm}^2$  for 80 seconds. The resultant cast film was coagulated into a membrane by placing it in a mixture of 1 volume acetone and 3 volumes water. This membrane was annealed at 130° for 30 min under restraint. After annealing, its flux was 802.8  $\text{hl}/\text{m}^2/\text{d}$  (1970  $\text{gal}/\text{ft}^2/\text{day}$ ) at 172 kPa (25 psi) and its bubble point was 495 kPa (72 psi). It contained 3.5% by weight poly(hydroxypropyl acrylate-co-tetraethylene glycol diacrylate). The membrane wet completely in less than 30 seconds and retained 90% of 0.07  $\mu\text{m}$  (.07u) beads when an aqueous suspension of these beads was filtered through it.

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The flux of the membranes was measured using ultrafiltration cells, graduate cylinders, and stopwatches. 43 mm diameter disks were cut from the membranes, wet with water, and positioned in the cells. The cells were filled with water and pressurized to 172 kPa (25 pounds per square inch (psi)) to drive the water across the membrane. A stopwatch was started as the pressure was applied. A reasonable volume of water, typically 10-30 ml, was collected; the volume in milliliters and the time to collect it, in minutes, were recorded. Milliliters per minute per square centimeter of membrane was converted to gallons per foot<sup>2</sup> per day (gfd).

The bubble point of the membrane is measured from the pressure required to displace isopropyl alcohol (IPA) from an IPA-wet membrane. A fluid-wet membrane will allow air to pass through it when the applied air pressure exceeds the capillary attraction of the fluid to the pore. The relation between the size of a fluid-wet cylindrical pore and the air pressure required to empty it ( $P$ , the bubble pressure for that cylindrical pore) is:

$$D = 4 \gamma \cos \theta / P$$

where  $D$  is the diameter of the pore,  $\theta$  is the contact angle, and  $\gamma$  is the surface tension of the wetting liquid. When measured bubble pressure can be empirically correlated to the size of real membrane pores it provides readily obtained estimates of the sizes of real, noncylindrical pores. One empirical method used to correlate bubble pressure with the pore sizes of the membranes of this invention is to determine the smallest particles that are retained by the membranes. The membrane are challenged with sub-micron size latex beads and the fraction of beads retained by the membrane are measured. If substantially all (>90%) of the beads are retained by the membrane, the largest pores are smaller than the average diameters of the latex beads.

The bubble point of the membrane is measured using a device similar to that described by Dadenhop et al, Membrane Science and Technology, J.E. Flynn, Ed., Plenum Press (1970). The membrane is positioned in the device and wet with IPA. Increasing air pressure is applied to the skin side of the membrane rapidly enough to prevent IPA-induced changes in morphology. Typically the applied pressure starts at 0 kPa (0 psi) and reaches 688 kPa (100 psi) within 2 minutes of wetting with IPA. The applied pressure sufficient to cause measurable amounts of air flow through the membrane is taken to be the bubble pressure of bubble point,  $P$ . In this variation of the bubble point test,  $P$  estimates the size of the largest membrane pores.

Thus the largest pores of the membrane described in Example 1 are smaller than about 0.07  $\mu\text{m}$  (.07  $\mu$ ), which corresponds to a bubble pressure (bubble point) of about 495 kPa (72 psi). As shown in the attached Figure.

### EXAMPLE II

This example shows the unexpected change in the properties of the membranes on annealing. Five grams of hydroxylpropyl acrylate (HPA), 1 gram of tetraethylene glycol deacrylate (TEGDA), and 4 grams of Darocure 1173 were added to 91.0 grams of a solution containing 14% poly(vinylidene fluoride) 5% LiCl in DMAc. Portions of the solution were cast separately into films 254  $\mu\text{m}$  (10 mils) thick onto a glass plate. Each film was exposed to ultraviolet light at an intensity of between about 0.2 and 0.6 mW/cm<sup>2</sup> (wavelength of maximum emission was 365 nm.) for 15 seconds immediately after casting. The irradiated films were coagulated with various non-solvents, washed, dried, fixed in a frame and annealed as summarized in Table I. Properties of these membranes before and after annealing are also given in Table I.

### EXAMPLE III

This example shows that the membranes of the invention are resistant to protein adsorption. Ten grams of HPA, 1 gram of TEGDA, 4 grams of Darocure 1173 initiator were added to 85.0 grams of a solution containing 14% poly(vinylidene fluoride) 5% LiCl in DMAc. The solution was cast in a film 254  $\mu\text{m}$  (10 mils) thick onto a glass plate and immediately exposed to ultraviolet light as in Example II for 2 minutes. The irradiated film was coagulated with a mixture of 1 part acetone and 3 parts water, washed, dried, fixed in a frame and annealed at 130° for 30 minutes. The membrane wet completely in less than 30 seconds. It had a flux of 1589 hl/m<sup>2</sup>/d (3900 gfd) at 172 kPa (25 psi) and a bubble point of 454 kPa (66 psi). The protein binding characteristics of the membrane were estimated by the following procedure. Samples of this membrane were soaked in 1% bovine serum albumin (BSA) overnight. Also, samples of nonadsorptive hydrophilic Durapore (TM), and highly adsorptive cellulose esters were soaked in BSA overnight. All unbound albumin was rinsed from the membranes. The samples were then soaked in Ponceau S red dye for 1 hour to color and bind protein, rinsed with 5% acetic acid to remove excess dye, rinsed again with distilled water, and allowed to dry. The amount of protein bound to the membranes was estimated qualitatively from the amount of color left after rinsing and drying. The membrane prepared in this example was visually similar to the nonadsorptive hydrophilic Durapore (TM) membranes in that both membranes were very faintly pink. The highly adsorptive cellulose ester membranes were much more intensely colored.

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### EXAMPLE IV

Ten grams of HPA, 0.6 grams of TEGDA, and 4 grams of Darocure 1173 were added to 84.9 grams of a solution containing 14% poly(vinylidene fluoride) 5% LiCl in DMAc. The solution was cast in a film 254  $\mu\text{m}$  (10 mils) thick onto a glass plate and immediately exposed to ultraviolet light as in Example II for 15 seconds. The irradiated film was coagulated with water, washed, dried, fixed in a frame and annealed at 130° for 30 minutes. The membrane wets completely in less than 30 seconds. It had a flux of 412  $\text{hl/m}^2/\text{d}$  (1010  $\text{gfd}$ ) at 172 kPa (25 psi) and a bubble point of 605 kPa (88 psi).

**TABLE I**  
**Effects of Annealing on Membrane Properties**

Sample	Coag- ulant	Annealing Conditions °C	Flux		Wetting Time Before Annealing	Wetting Time After Annealing
			Before Annealing	After Annealing		
1. (1)		(1)	650	3200	1 minute	1 sec
2. (1)		(2)	380	2300	phobic	12 sec
3. (2)		(2)	2500	3620	phobic	5 sec

Sample	Bubble Point	
	Before Annealing	After Annealing
1	71	47
2	65	76
3	62	54

Coagulants--(1) H<sub>2</sub>O, (2) NMP; H<sub>2</sub>O 1:3  
 Annl. Conditions--(1) 150°, 30 min.; (2) 130°, 30 min.  
 Flux is in gallons/foot<sup>2</sup>/day at 25 pounds per square inch.  
 Bubble point is in pounds per square inch.

Note:

$$1 \frac{\text{gallon}}{\text{foot}^2/\text{day}} \hat{=} 0.4075 \frac{\text{ml}}{\text{cm}^2/\text{d}}$$

$$1 \text{ pound per square inch (psi)} \hat{=} 6.878 \text{ kPa}$$

Claims

1. A porous membrane having a water wettable surface which membrane comprises a porous semi-interpenetrating polymer network of a hydrophobic fluorinated hydrocarbon polymer and a hydrophilic cross-linked polymer, the interpenetrating polymer network being formed by synthesising and crosslinking the hydrophilic polymer in the immediate presence of the hydrophobic polymer, the entire surface of the membrane including the pore surface being formed from said hydrophobic polymer in semi-crystalline form and said hydrophilic polymer.
2. The porous membrane of claim 1 wherein said membrane has a maximum pore size between about 0.01 and 0.1  $\mu\text{m}$  (microns).
3. The porous membrane of claim 2 wherein said membrane has an isopropyl alcohol bubble point of between about 275 kPa (40 psi) and about 963 kPa (140 psi), a water flux of above about 1426  $\text{hl}/\text{m}^2/\text{d}$  (3500 gallons per square foot per day) at 172 kPa (25 psi) for a membrane having a bubble point of about 275 kPa (40 psi), a water flux of above about 407.5  $\text{hl}/\text{m}^2/\text{d}$  (1000 gallons per square foot per day) at 172 kPa (25 psi) for a membrane having a bubble point of about 550 kPa (80 psi), and a water flux above about 407.5  $\text{hl}/\text{m}^2/\text{d}$  (1000 gallons per square foot per day) at 172 kPa (25 psi) for a membrane having a bubble point of about 963 kPa (140 psi).
4. The membrane of any one of claims 1, 2, or 3 wherein the hydrophobic polymer is polyvinylidene fluoride.
5. The porous membrane of any one of claims 1, 2 or 3 wherein said hydrophilic polymer is formed from an hydroxyalkyl acrylate.
6. A process for forming a porous membrane having an entirely water wettable surface including the pore surface, said membrane being formed of a semi-interpenetrating polymer network of a hydrophobic polymer and a cross-linked hydrophilic second polymer, the entire surface of the membrane including the pore surface being formed from said hydrophobic polymer in semi-crystalline form and said hydrophilic polymer, which comprises:
  - (a) forming a solution of said hydrophobic polymer, a monomeric composition being a precursor of said hydrophilic polymer, a crosslinking agent for said monomeric composition and a photoinitiator for said monomer composition,
  - (b) casting said solution on a substrate,
  - (c) exposing said cast solution to ultraviolet radiation to polymerize and cross-link said monomeric composition, thereby effecting formation of an semi-interpenetrating polymeric network in solution,
  - (d) coagulating said cast solution,
  - (e) removing solvent from said coagulated solution to form a dried porous membrane, and
  - (f) annealing said dried porous membrane by a heat treatment in order to increase crystallinity of the hydrophobic polymer and to thereby increase the water wettability of the entire surface of said membrane, including the pore surface.
7. The process of claim 6 wherein said dried porous membrane is restrained to prevent shrinkage during annealing.
8. The process of any one of claims 6 or 7 wherein said annealing step is conducted at a temperature between about 130°C and about 160°C for a time between about 20 minutes and 60 minutes.
9. The process of any one of claims 6 or 7 wherein said hydrophobic polymer is a fluorinated hydrocarbon polymer.
10. The process of any one of claims 6 or 7 wherein said hydrophobic polymer is a polyvinylidene fluoride.
11. The process of any one of claims 6 or 7 wherein said monomeric composition is an hydroxyalkyl acrylate.
12. The process of any one of claims 6 or 7 wherein said porous membrane has a maximum pore size between about 0.01 and 0.1  $\mu\text{m}$  (micron) and has an isopropyl alcohol bubble point of between about 275 kPa (40 psi) and 963 kPa (140 psi), a water flux of above about 1426  $\text{hl}/\text{m}^2/\text{d}$  (3500 gallons per square foot per day) at 172 kPa (25 psi)



for a membrane having a bubble point of about 275 kPa (40 psi), a water flux of above about 407.5 hl/m<sup>2</sup>/d (1000 gallons per square foot per day) at 172 kPa (25 psi) for a membrane having a bubble point of about 550 kPa (80 psi) and a water flux of above about 407.5 hl/m<sup>2</sup>/d (1000 gallons per square foot per day) at 172 kPa (25 psi) for a membrane having a bubble point of about 963 kPa (140 psi).

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# Patentansprüche

1. Poröse Membran mit wasserbenetzbarer Oberfläche, umfassend ein poröses semiinterpenetrierendes Polymer-  
netzwerk eines hydrophoben fluorierten Kohlenwasserstoffpolymers und eines hydrophilen vernetzten Polymers,  
wobei das interpenetrierende Polymernetzwerk durch Synthese und Vernetzen des hydrophilen Polymers in unmittelbarer Gegenwart des hydrophoben Polymers gebildet ist und die gesamte Oberfläche der Membran einschließlich der Porenoberfläche aus dem hydrophoben Polymer in semikristalliner Form und dem hydrophilen Polymer besteht.
2. Poröse Membran nach Anspruch 1, die eine maximale Porengröße zwischen etwa 0,01 und 0,1 µm (Mikron) aufweist.
3. Poröse Membran nach Anspruch 2, die einen Isopropanol-Blasenpunkt zwischen etwa 275 kPa (40 psi) und etwa 963 kPa (140 psi), einen Wasserfluß von oberhalb etwa 1426 hl/m<sup>2</sup>/d (3 500 Gallonen/Quadratfuß/Tag) bei 172 kPa (25 psi) für eine Membran eines Blasenpunkts von etwa 275 kPa (40 psi), einen Wasserfluß von oberhalb etwa 407,5 hl/m<sup>2</sup>/d (1 000 Gallonen/Quadratfuß/Tag) bei 172 kPa (25 psi) für eine Membran eines Blasenpunkts von etwa 550 kPa (80 psi) und einen Wasserfluß von oberhalb etwa 407,5 hl/m<sup>2</sup>/d (1 000 Gallonen/Quadratfuß/Tag) bei 172 kPa (25 psi) für eine Membran eines Blasenpunkts von etwa 963 kPa (140 psi) aufweist.
4. Membran nach einem der Ansprüche 1, 2 oder 3, wobei das hydrophobe Polymer aus Polyvinylidenfluorid besteht.
5. Poröse Membran nach einem der Ansprüche 1, 2 oder 3, wobei das hydrophile Polymer aus einem Hydroxyalkylacrylat gebildet ist.
6. Verfahren zur Bildung einer porösen Membran einer vollständig wasserbenetzbaren Oberfläche einschließlich der Porenoberfläche, wobei die Membran aus einem semiinterpenetrierenden Polymernetzwerk aus einem hydrophoben Polymer und einem vernetzten hydrophilen zweiten Polymer gebildet ist und die gesamte Oberfläche der Membran einschließlich der Porenoberfläche aus dem hydrophoben Polymer in semikristalliner Form und dem hydrophilen Polymer besteht, durch
  - (a) Ausbilden einer Lösung des hydrophoben Polymers, einer monomeren Masse, bestehend aus einem Vorläufer des hydrophilen Polymers, eines Vernetzungsmittels für die monomere Masse und eines Photoinitiators für die monomere Masse;
  - (b) Vergießen der Lösung auf ein Substrat;
  - (c) Einwirkenlassen von UV-Strahlung auf die vergossene Lösung zur Polymerisation und Vernetzung der monomeren Masse unter Ausbildung eines semiinterpenetrierenden polymeren Netzwerks in der Lösung;
  - (d) Koagulieren der vergossenen Lösung;
  - (e) Entfernen von Lösungsmittel aus der koagulierten Lösung zur Bildung einer getrockneten porösen Membran und
  - (f) Altern der getrockneten porösen Membran durch Wärmebehandlung zur Erhöhung der Kristallinität des hydrophoben Polymers unter gleichzeitiger Erhöhung der Wasserbenetzbarkeit der gesamten Oberfläche der Membran einschließlich der Porenoberfläche.
7. Verfahren nach Anspruch 6, wobei die getrocknete poröse Membran festgehalten wird, um eine Schrumpfung während des Alterns zu verhindern.
8. Verfahren nach einem der Ansprüche 6 oder 7, wobei etwa 20 min bis 60 min bei einer Temperatur zwischen etwa 130°C und etwa 160°C gealtert wird.

9. Verfahren nach einem der Ansprüche 6 oder 7, wobei das hydrophobe Polymer aus einem fluorierten Kohlenwasserstoffpolymer besteht.
10. Verfahren nach einem der Ansprüche 6 oder 7, wobei das hydrophobe Polymer aus einem Polyvinylidenfluorid besteht.
11. Verfahren nach einem der Ansprüche 6 oder 7, wobei die monomere Masse aus einem Hydroxyalkylacrylat besteht.
12. Verfahren nach einem der Ansprüche 6 oder 7, wobei die poröse Membran eine maximale Porengröße zwischen etwa 0,01 und 0,1 µm (Mikron) sowie einen Isopropanol-Blasenpunkt zwischen etwa 275 kPa (40 psi) und etwa 963 kPa (140 psi), einen Wasserfluß von oberhalb etwa 1426 hl/m<sup>2</sup>/d (3 500 Gallonen/Quadratfuß/Tag) bei 172 kPa (25 psi) für eine Membran eines Blasenpunkts von etwa 275 kPa (40 psi), einen Wasserfluß von oberhalb etwa 407,5 hl/m<sup>2</sup>/d (1 000 Gallonen/Quadratfuß/Tag) bei 172 kPa (25 psi) für eine Membran eines Blasenpunkts von etwa 550 kPa (80 psi) und einen Wasserfluß von oberhalb etwa 407,5 hl/m<sup>2</sup>/d (1 000 Gallonen/Quadratfuß/Tag) bei 172 kPa (25 psi) für eine Membran eines Blasenpunkts von etwa 963 kPa (140 psi) aufweist.

#### Revendications

1. Membrane poreuse ayant une surface pouvant être mouillée par l'eau, laquelle membrane comprend un réseau semi-interpénétré poreux de polymères qui est constitué par un polymère hydrocarboné fluoré hydrophobe et un polymère réticulé hydrophile, le réseau interpénétré de polymères étant formé par synthèse et réticulation du polymère hydrophile en présence immédiate du polymère hydrophobe, la surface entière de la membrane qui comprend la surface poreuse étant formée à partir dudit polymère hydrophobe sous une forme semi-cristalline et dudit polymère hydrophile.
2. Membrane poreuse conforme à la revendication 1, dans laquelle ladite membrane a une taille de pore maximum comprise entre environ 0,01 et 0,1 µm (micromètre).
3. Membrane poreuse conforme à la revendication 2, dans laquelle ladite membrane a un point de bulle dans l'alcool isopropylique compris entre environ 275 kPa (40 psi) et environ 963 kPa (140 psi), un flux d'eau supérieur à environ 1426 hl/m<sup>2</sup>/j (3500 gallons par pied carré par jour) sous 172 kPa (25 psi) pour une membrane ayant un point de bulle d'environ 275 kPa (40 psi), un flux d'eau supérieur à environ 407,5 hl/m<sup>2</sup>/j (1000) gallons par pied carré par jour sous 172 kPa (25 psi) pour une membrane ayant un point de bulle d'environ 550 kPa (80 psi), et un flux d'eau supérieur à environ 407,5 hl/m<sup>2</sup>/j (1000 gallons par pied carré par jour) sous 172 kPa (25 psi) pour une membrane ayant un point de bulle d'environ 963 kPa (140 psi).
4. Membrane conforme à l'une quelconque des revendications 1, 2, ou 3, dans laquelle le polymère hydrophobe est le poly(fluorure de vinyldène).
5. Membrane conforme à l'une quelconque des revendications 1, 2, ou 3, dans laquelle le polymère hydrophile est formé à partir d'un acrylate d'hydroxyalkyle.
6. Procédé qui consiste à former une membrane poreuse ayant une surface pouvant être mouillée entièrement par l'eau, comprenant la surface poreuse, ladite membrane étant formée par un réseau semi-interpénétré de polymères qui est constitué par un polymère hydrophobe et un second polymère hydrophile et réticulé, la surface entière de la membrane qui comprend la surface poreuse étant formée à partir dudit polymère hydrophobe sous une forme semi-cristalline et dudit polymère hydrophile, lequel procédé comprend
  - (a) le fait de former une solution constituée par ledit polymère hydrophobe, une composition de monomère qui est un précurseur dudit polymère hydrophile, un agent de réticulation pour ladite composition de monomère et un photoamorceur pour ladite composition de monomère,
  - (b) le fait de couler ladite solution sur un substrat,
  - (c) le fait d'exposer ladite solution coulée à un rayonnement ultraviolet afin de polymériser et de réticuler ladite composition de monomère, ce qui permet d'obtenir la formation d'un réseau semi-interpénétré de polymères en solution,
  - (d) le fait de coaguler ladite solution coulée,
  - (e) le fait d'éliminer le solvant de ladite solution coagulée afin de former une membrane poreuse desséchée, et

(f) le fait de recuire ladite membrane poreuse desséchée au moyen d'un traitement thermique afin d'augmenter la cristallinité du polymère hydrophobe, ce qui permet d'augmenter la mouillabilité par l'eau de la surface entière de ladite membrane, qui comprend la surface poreuse.

- 5 7. Procédé conforme à la revendication 6, dans lequel on soumet ladite membrane poreuse desséchée à une contrainte afin d'empêcher un retrait au cours du recuit.
8. Procédé conforme à l'une quelconque des revendications 6 ou 7, dans lequel on effectue ladite étape du recuit à une température comprise entre environ 130° C et environ 160° C pendant une durée comprise entre environ 20  
10 minutes et 60 minutes.
9. Procédé conforme à l'une quelconque des revendications 6 ou 7, dans lequel ledit polymère hydrophobe est un polymère hydrocarboné fluoré.
- 15 10. Procédé conforme à l'une quelconque des revendications 6 ou 7, dans lequel ledit polymère hydrophobe est un poly(fluorure de vinylidène).
11. Procédé conforme à l'une quelconque des revendications 6 ou 7, dans lequel la composition de monomère est un acrylate d'hydroxyalkyle.
- 20 12. Procédé conforme à l'une quelconque des revendications 6 ou 7, dans lequel ladite membrane poreuse a une taille maximum de pore comprise entre environ 0,01 et 0,1 µm (micromètre) et a un point de bulle dans l'alcool isopropylique compris entre environ 275 kPa (40 psi) et environ 963 kPa (140 psi), un flux d'eau supérieur à environ 1426 hl/m<sup>2</sup>/j (3500 gallons par pied carré par jour) sous 172 kPa (25 psi) pour une membrane ayant un point de bulle  
25 d'environ 275 kPa (40 psi), un flux d'eau supérieur à environ 407,5 hl/m<sup>2</sup>/j (1000 gallons par pied carré par jour) sous 172 kPa (25 psi) pour une membrane ayant un point de bulle d'environ 550 kPa (80 psi), et un flux d'eau supérieur à environ 407,5 hl/m<sup>2</sup>/j (1000 gallons par pied carré par jour) sous 172 kPa (25 psi) pour une membrane ayant un point de bulle d'environ 963 kPa (140 psi).

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